Chapter 4

Results and Discussion
4.1. Photocatalytic property of metal doped Strontium Titanate (SrTiO$_3$) Nanoparticles

(I) Efficient Degradation of Methylene Blue Dye over Highly Reactive Cu doped Strontium Titanate (SrTiO$_3$) Nanoparticles Photocatalyst under Visible Light

4.1.1. INTRODUCTION
The discovery by Fujishima and Honda on electrolysis of water into H$_2$ and O$_2$ by photosensitization of TiO$_2$ semiconductor has recently received much attention, which opens new era for converting solar energy into useful chemical energy and photo-catalytic degradation of non-biodegradable dyes mediated over semiconductor photocatalyst.\textsuperscript{1} The effective utilization of clean, safe, and abundant solar energy will lead to the promising solution not only for energy crisis and related issues but will also have an impact on the exhaustion of natural energy resources which causes environmental pollution.\textsuperscript{2-5} In general, many dyes containing nitrogen (N) atom undergo reductive anaerobic degradation to produce the carcinogenic products. These discharged products are very hazardous for aquatic and human life and causes serious consequences to the surrounding ecosystem.\textsuperscript{6,7} Methylene Blue is a widely used dye in leather and cotton industries, which causes environmental hazards and imbalances non-aesthetic pollution, eutrophication in the aquatic life. The physical methods like adsorption, biodegradation and chemical degradation have been used for waste water treatment. However, these methods transfer dyes from liquid to solid phase causing secondary pollution and require further treatment. Hence, it is essential to develop an effective method for efficient degradation of non-biodegradable dyes to check the aquatic pollution because most of the dyes are resistant to biodegradation; they are
not easily removed in biological water treatment plant. Heterogeneous photocatalysis is commonly employed to eliminate hazardous waste water materials especially organic compounds to less toxic materials like carbon dioxide, water and less harmful materials.\(^8\)\(^-\)\(^^{10}\)

In the recent years, the perovskite type metal oxides with general formula ABO\(_3\) have been investigated due to their diverse and exotic properties. The oxygen and the doping with novel foreign materials in perovskite materials show the efficient photocatalyst towards many photocatalytic activities such as dye degradation, water splitting and other photo conversion reactions.\(^{11}\)

Recently, strontium titanate (SrTiO\(_3\)) is an important known material, which is capable for the decomposition of water into H\(_2\) and O\(_2\) and mineralization of organic pollutants under UV light irradiation.\(^{12}\),\(^{13}\) Due to its large band gap 3.2eV, it could only response to UV light. In order to explore its visible light response, the doping of foreign element into SrTiO\(_3\) that creates a new acceptor level just above the Fermi level in the SrTiO\(_3\) semiconductor and results the visible light active photocatalysts which contributes about 48% of solar spectrum.\(^{14}\)\(^-\)\(^^{17}\)

Various methods have been reported for the synthesis of SrTiO\(_3\).\(^{18}\),\(^{19}\) A solid state reaction route (SSR) is commonly used for synthesis of SrTiO\(_3\), but it requires high temperature which causes non-stoichiometry and uncontrolled growth of materials.\(^{20}\)\(^-\)\(^^{22}\) So far, it is difficult to synthesize SrTiO\(_3\) with exact stoichiometry. Moreover, there are several drawbacks of SSR such as non-stoichiometry, segregation of one or more compounds and uncontrolled growth. On the other hand, the solution methods like sol-gel, hydrothermal process have known for the ease of to control the size and morphology of metal oxides nanomaterials. Here, we use a facile simple sol-gel method to synthesized Cu doped SrTiO\(_3\) nanoparticles and study the photocatalytic activity toward the degradation of Mehylene blue dye under visible light.
4.1.2. EXPERIMENTAL SECTION

4.1.2.1. Photocatalyst Preparation

All the chemicals are analytical grade and used without further purification. The chemicals used for the synthesis of Cu-doped SrTiO$_3$ nanoparticles were as follows; the Strontium acetate Sr(CH$_3$COO)$_2$ (99.8% Sigma-Aldrich), Copper acetate (99.8% Sigma-Aldrich), Titanium isopropoxide (TTIP, Sigma-Aldrich 98.9%), Citric acid (99.8% Sigma-Aldrich), Ethyl alcohol (99.8% Sigma-Aldrich) and Ethylene glycol (99.8% Sigma-Aldrich). The Cu doped SrTiO$_3$ nanoparticles were synthesized by sol-gel method. In this process, titanium and strontium precursors solutions were prepared and designated as A and B solution, respectively. Solution A was prepared by dissolving 6.5 mL of TTIP and 6.7 mL ethylene glycol into 80 mL ethanol under continuous stirring for 30 min. Then 6.3 g of citric acid was dissolved into 10 mL deionized (DI) water and added slowly into the solution A. The citric acid acts as a chelating agent in this reaction. In a separate beaker, 0.275g copper acetate was dissolved in 10 mL DI water under continuous stirring and get light blue colored solution then this copper acetate solution was gradually added into the Sr(CH$_3$COO)$_2$ solution (4.12 g dissolved in 25 mL DI water) under continuous stirring to get solution B.

Afterward, the solution B was mixed with solution A and the resultant solution was then transferred into three-necked round bottom flask and refluxed for 8 h at 80 °C. After completion of the reaction, the pale blue white precipitates were obtained. It was repeatedly washed with DI water and alcohol and dried in oven at 70 °C. The obtained pale blue white powder was further calcined at 600 °C for 5 h. The schematic procedure for synthesis is summarized in the flow chart illustration of Figure 4.1.1.
Figure 4.1.1. Flow Chart for synthesizing Cu doped SrTiO$_3$ nanoparticles.

1. Ethylene Glycol
2. Titania Isopropoxide
3. Three Neck Flask (solution A)
4. Strontium acetate
5. Ti(OC$_3$H$_7$)$_4$ + E.G + C$_2$H$_5$OH + C.A
6. Cupper acetate
7. Metal Citrate complex
8. GEL
9. Calcined at 600 °C for 5 h
10. Cu doped SrTiO$_3$
4.1.2.2. Photocatalytic Activity Measurement

The photocatalytic activity of Cu/SrTiO₃ was measured in three necked Pyrex flask reactor under the illumination using 300 W Xe arc lamp (λ>330nm, Toshiba SHLS-1002). A cutoff filter was placed in between the irradiation source and photoreactor vessel to eliminate radiation below 380 nm. Firstly, 15 mg of Cu/SrTiO₃ photocatalysts was introduced in 10 ppm of aqueous MB dye solution under continuous stirring. Prior to illumination, suspension was continuously stirred for about 1 hour to develop adsorption–desorption equilibrium between MB dye and photocatalyst in the dark condition. Then, the solution was exposed to visible light illumination under continuous stirring. The sample was periodically taken after every 10 minutes and then centrifuged at 12,000 rpm to separate out the Cu/SrTiO₃ powder and finally, the absorbance of decomposed dye solution was measured by UV-Visible Spectrophotometer (PerkinElmer Model 750, USA) to elucidate the degradation rate.

The pseudo-first order rate kinetics was followed for photocatalytic degradation of MB dye and rate constant value was determined by the following relation;

\[
\ln\left(\frac{C_o}{C}\right) = kt \\
(4.1.1)
\]

Where k value was calculated from graph between \(\ln(C_o/C)\) vs time interval, \(C_o\) and \(C\) denote the MB dye concentration at \(t=0\) and \(t = t\), respectively.

4.1.2.3. Characterizations

The crystalline properties of prepared Cu/SrTiO₃ photocatalyst was identified by X-ray diffractometer (XRD, Philips X’Pert with Cu Kα, \(\lambda =0.15419\) nm with scanning rate 4°/min) in the range of 20–80°. The surface morphology of as prepared Cu/SrTiO₃ nanoparticles was recorded by scanning electron microscopy.
(SEM, INCAPentaFET-x3) equipped with energy dispersive X-ray (EDX), respectively. The optical properties and the band gap studies were performed by using UV-Vis diffused reflectance spectrum (UV-DRS, Perkin Elmer Lambda 35).

4.1.3. RESULTS AND DISCUSSION

Figure 4.1.2. shows the FESEM images and EDX analysis of as-synthesized Cu/SrTiO$_3$ nanoparticles. The uniform small spherical particles are observed which have the average particle size of 60-75 nm (Figure 4.1.2(a)). It indicates that the uniform Cu/SrTiO$_3$ nanoparticles are synthesized by simple sol-gel method. The elemental analysis (Figure 4.1.2(b)) has been carried out to explain the presence of Cu element in SrTiO$_3$. From EDX results, the atomic percentages of Sr/Ti/O/Cu are as 19%/18%/60%/2%, respectively. The presence of Cu reveals that Cu doping is successfully occurred without disturbing the basic structure of ABO$_3$ type of SrTiO$_3$.

The X-ray diffraction (XRD) patterns of the as-synthesized Cu/SrTiO$_3$ are shown in Figure 4.1.3. It possesses the dominant diffraction peaks at $2\theta$ angle as 32.4$^\circ$, 39.8$^\circ$, 47.2$^\circ$, 57.8$^\circ$, 67.9$^\circ$ and 78.9$^\circ$, representing the indices of (110), (111), (200), (211), (220) and (310) lattice planes, respectively. The XRD patterns are well matched with the JCPDS card number 350734. The obtained XRD patterns reveals that as-synthesized Cu/SrTiO$_3$ with perovskite type structure belongs to cubic space group P-m3m with lattice constant $a= 3.92$ Å. It is reported that the ionic radii of six-coordinated Cu$^{2+}$ ion (0.61 Å) is almost similar to Ti$^{4+}$ ion (0.61 Å), but smaller than that of Sr$^{2+}$ ion (1.26Å). 23 It means that Cu$^{2+}$ ion easily replaces Ti$^{4+}$ ion and is fully incorporated in SrTiO$_3$. 

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**Figure 4.1.2.** FE-SEM image (a) and energy dispersive X-ray and (b) spectrum of Cu/SrTiO nanoparticles.

**Figure 4.1.3.** X-ray diffraction pattern of Cu doped SrTiO$_3$ nanoparticles obtained by calcinations at 600 °C for 5 h.
Figure 4.1.4 shows the UV-Vis diffused reflectance spectrum of as-synthesized Cu/SrTiO$_3$ nanoparticles. The absorption edges of as synthesized Cu/SrTiO$_3$ exhibit the significant red shift which approaches the visible light region. The band gap energy of synthesized Cu/SrTiO$_3$ can be calculated from the optical absorption edge onset ($\lambda$) of reflectance spectrum using band gap energy relation of $E(\text{eV}) = \frac{1240}{\lambda}$ (nm), where $\lambda$ is absorption edge and $E$ is band gap energy of synthesized Cu/SrTiO$_3$. It is seen that the absorption edge is obtained to ~420 nm which is shifted to higher absorption edge as compared to previous report based on SrTiO$_3$ nanoparticles (392 nm). Generally, the band gap energy of SrTiO$_3$ is estimated to 3.2 eV at ~392 nm and it is higher than that of the band gap of synthesized Cu/SrTiO$_3$ nanoparticles i.e. 2.96 eV at 420 nm. Noticeably, the change in the band gap clearly suggests the extent of shifting in absorption edge caused by the introduction of Cu dopant. From figure 4.1.4, it can be seen that synthesized Cu/SrTiO$_3$ nanoparticles display two absorption edges i) the strong absorption edge at 420 nm is ascribed to transition of 3d electron of Cu$^{2+}$ ions to Ti$^{4+}$ which belongs to the fully allowed, charge-transfer transition and ii) the weak broad absorption edge at ~520nm onwards arises from the d-d transition of $^4A_2$ to $^4T_2$ in Cu$^{2+}$ ions in octahedral system.

It is well known that photocatalytic activity of a semiconductor is related to its band gap structure. The doping of Cu into SrTiO$_3$ may generate a new donor level just above the fermi level of SrTiO$_3$ due to the reduction in the band gap. The Cu doping results in an upward shift for the fermi level and a downward shift for the conduction band of SrTiO$_3$, this lowers the band gap energy of SrTiO$_3$ which was calculated to be 2.96 eV. It is assumed that the special electronic structure of synthesized Cu/SrTiO$_3$ nanoparticle might facilitate the mobility of photoexcited holes to surface of synthesized catalyst and initiate the photocatalytic reactions in the visible region.
Figure 4.1.4. UV-Vis DRS spectrum of Cu/SrTiO$_3$ nanoparticles.
The photocatalytic activity of as-synthesized Cu/SrTiO$_3$ nanoparticles was demonstrated over degradation of methylene blue (MB) dye under visible light irradiation as shown in Figure 4.1.5. It shows (a) the UV-Vis spectra of decomposed MB dye and exhibits the maximum absorption wavelength ($\lambda_{\text{max}}$) at 661nm. The intensities of absorption peaks are decreased as increasing the photocatalytic reaction time (0-120 min) under visible light irradiation. However, no change in colour of MB dyes solution is observed when reaction has performed under dark for one hour, indicating that the catalysts and light irradiation play crucial role to degrade the MB dye. The synthesized Cu/SrTiO$_3$ catalysts considerably degrade the MB dye by ~66% within 120 min under visible light irradiation. Figure 4.1.5(b) shows the extent of degradation rate in terms of $\ln(C_0/C)$ vs time interval. The MB dye gradually decomposes up to 66% with the increase of time interval from 0 to 120 min. The kinetics of degradation of MB is evaluated using figure 4.1.5(b) and it shows an apparent first order in agreement with a general Langmuir – Hinshelwood mechanism as expressed by:

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \quad (4.1.2)$$

Where, \(r\) is degradation rate of reactant (mg/l min), \(C\) the concentration of reactant (mg/l), \(t\) the illumination time, \(K\) is the adsorption coefficient of reactant (l/mg), and \(k\) represents the reaction rate constant (mg/l min). When the initial concentration \(C_0\) is 10 ppm, \(K\) value is almost fixed for a particular dye, and then the above equation can be simplified to an apparent first order equation as follows:

$$\ln(C_0/C) = kKt \approx k_{\text{app}}t \quad (4.1.3)$$

It is found that a plot between $\ln(C_0/C)$ versus time represents a straight line, the slope of linear regression equals the apparent first order rate constant $k_{\text{app}}$ (0.0016
min\(^{-1}\)) which is consistent with the reported first order reaction. Additionally, Figure 4.1.6(a) reveals the extent of discoloration of MB dye in the form of pie chart of degradation reaction versus time interval. The major degradation of MB dye occurs first 40 min of reaction under visible light illumination and afterward the extent of degradation has accelerated in every time interval at the moderate rate. It is reported that the dye molecules reached the excited state from where a series of photocatalytic reaction occurs at the surface of photocatalysts Cu/SrTiO\(_3\).\(^{30-34}\)

The illustrative mechanism has proposed to understand the degradation of MB dye over the surface of Cu/SrTiO\(_3\) photocatalyst under visible light irradiation as depicted in figure 4.1.6(b). It involves several steps to precede the photocatalytic degradation of MB dye under visible irradiation as follows;

(i) Firstly, it generates electron/hole pairs due to migration of electron (\(\text{e}^-\)) from fermi level to conduction band of Cu/SrTiO\(_3\),

\[
\text{Cu/SrTiO}_3 + \text{hv} \rightarrow \text{e}_{\text{cb}}^- + \text{h}_{\text{vb}}^+
\]

(4.1.4)

(ii) \(\text{e}^-\) in conduction band reduces the O\(_2\) molecule and generates superoxide radicals at Cu/SrTiO\(_3\) surface,

\[
\text{O}_2^- + \text{e}_{\text{cb}}^- \rightarrow \text{O}_2'^-
\]

(4.1.5)

(iii) The hole in valence band reacts with OH\(^-\) that adsorbed on the surface forming the OH\(^-'\) radicals,

\[
\{\text{H}_2\text{O}\leftrightarrow\text{H}^+ + \text{OH}^-\}_{\text{adsorbed}} + \text{h}_{\text{vb}}^+ \rightarrow \text{H}^+ + \text{OH}'
\]

(4.1.6)

(iv) Neutralization of O\(_2'^-\) by protons,
\[ \text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- \]  

(4.1.7)

(v) The HO$_2^-$ radicals combine together at the surface of Cu/SiTiO$_3$ which leads to the formation of H$_2$O$_2$

\[ 2\text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  

(4.1.8)

(vi) Decomposition of H$_2$O$_2$ and second reduction of oxygen,

\[ \text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{OH}^- + \text{OH}^- \]  

(4.1.9)

The initial step of degradation of MB can be ascribed to the cleavage of the bonds of C-S$^+$=C functional groups in MB dye that leading to the generation of sulfate ions. The overall reaction can be summarized as:

\[ \text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+ + 10\text{OH}^- + \text{visible light} \rightarrow 16\text{CO}_2 + 3\text{NO}_3^- + \text{SO}_4^{2-} + 6\text{H}^+ + 57\text{H}_2\text{O} \]  

(4.1.10)

From the UV-DRS results, the creation of donor level just above the valence band originated by the addition of Cu impurity into the SrTiO$_3$ lattice, which facilitates the mobility of photoinduced charge carriers and thus enhances the photocatalytic activity of as-synthesized Cu/SrTiO$_3$ nanoparticles. In addition, the doping of Cu$^{2+}$ ions has been affirmed to introduce more oxygen vacancies in the crystal lattice and surface of SrTiO$_3$, while oxygen vacancies favor the adsorption of H$_2$O and formation of surface oxy-radicals over the surface of catalysts which might increase the degradation of MB under visible light irradiation. Therefore, the as-synthesized Cu/SrTiO$_3$ nanoparticles show the effective photocatalysts for the
degradation of MB dye under the visible light irradiation which delivers a simple and green heterogeneous photocatalytic approach for the degradation of hazardous organic pollutants.

**Figure 4.1.5** (a) The UV-Vis absorbance spectral changes of MB dye on Cu/SrTiO$_3$ with visible light irradiation and (b) Kinetics of MB degradation reaction in first order liner plot $\ln C_0/C$ vs time interval,

![Figure 4.1.5](image)

**Figure 4.1.6** (a) Extent of degradation of MB in every successive time interval and (b) Mechanistic diagram of degradation of MB dye under visible light over Cu/SrTiO$_3$. 

![Figure 4.1.6](image)
4.1.4. CONCLUSION

In summary, the highly crystalline Cu/SrTiO$_3$ nanoparticles are successfully synthesized by modified sol-gel method with citric acid as a chelating agent in ethylene glycol solution system and utilized as photocatalysts for the degradation of MB dye. The morphological properties and elemental analysis reveal that Cu$^{2+}$ can easily replace Ti$^{4+}$ ion in the ABO$_3$ type structure of SrTiO$_3$ due to the similar size of Cu$^{2+}$ ion and Ti$^{4+}$ ion. The red shift in the UV-DRS spectrum results the lowering of band gap energy of bare SrTiO$_3$ from 3.2 eV to 2.96 eV in Cu/SrTiO$_3$, leading the photo response of Cu/SrTiO$_3$ towards the visible region. The distribution of Cu$^{2+}$ ions may favor the separation of photogenerated electrons and holes by trapping under visible light irradiation. The photocatalytic application of as synthesized Cu/SrTiO$_3$ nanoparticles over MB dye reveals the extent of degradation by ~66% within 120 min under visible light irradiation. The MB dye degradation follows the first order mechanism and rate constant of this reaction has been calculated to be 0.0016 min$^{-1}$. 
References


4.2. ZnO nanomaterials: Growth, Properties and Photocatalytic Applications

4.2.(I). “Facile synthesis of ZnO nanoparticles by simple solution method with potential photocatalytic activity for dye degradation”

4.2.(I).1. INTRODUCTION

The wastes from the textile and dye industries are highly hazardous to aquatic living and human being because they cause the serious damage to the surrounding environment. 1, 2 Especially, the colored organics induce the environmental hazards, and imbalance non-aesthetic pollution and eutrophication in the aquatic life. 3 Among various techniques, the heterogeneous photocatalysis is popularly employed process to eliminate hazardous waste materials especially organic compounds to less toxic or less harmful materials. 4 Recently, the metal oxide semiconductors have shown the good photocatalytic activity towards the degradation of harmful organics into less harmful molecules under light illumination.
ZnO semiconductors with direct wide band gap ($E_g=3.37\text{eV}$) are highly explored n-type semiconductor owing to its high electron-hole binding energy (60 meV), high thermo-mechanical stability, good piezoelectric and optoelectronic properties. Moreover, ZnO semiconductors are known as the excellent material for the fabrication of various efficient electronic, optoelectronic devices, photovoltaic devices and photocatalysis. Moreover, ZnO is also known as a promising material for spintronics because of its ferromagnetic properties. Recently, ZnO nanomaterials applications in photocatalysis have received a great deal of interest because of its impressive catalytic activity and quantum efficiency than that of widely used TiO$_2$ nanomaterials. So far, various ZnO nanostructures have been used to degrade the harmful dyes into less harmful chemicals by photocatalytic reaction under UV light illumination. Sun et al. and Kuo et al. demonstrated the photo-catalytic degradation of Methylene Blue (~94%) in 5h and Rohdamine-B (~94%) in 300 min under UV light illumination over the surface of ZnO nanobelts and ZnO nanowires on Silicon wafer with assistance of SnO$_2$/Sn respectively.

In this part of chapter, a facile solution method is used to synthesize ZnO nanoparticles (NPs) at relatively low temperature using zinc acetate and oxalic acid and utilizes the photocatalyst for the degradation of Rhodamine B (RhB) dye. The synthesized ZnO nanoparticles have been extensively characterized in terms of morphology, structural, crystalline and photocatalytic properties.

4.2.(I).2. EXPERIMENTAL

For the synthesis of ZnO NPs, zinc acetate (0.05M) and oxalic acid (0.1M) solutions were prepared separately in deionized water under continuous stirring at room temperature. Freshly prepared oxalic acid solution was added drop wise into
zinc acetate solution under constant stirring and finally transferred into a three necked round bottom flask. The resultant solution was heated at 80 °C for 8h. After completion of reaction, the white color precipitate was obtained and washed repeatedly with methanol, deionized water and finally dried at 60 °C.

The photocatalytic activity of ZnO NPs towards the degradation of RhB dye was carried out in Pyrex flask type reactor under the UV illumination using xenon arc lamp (Thoshiba, SHLS-1002). For the effective degradation of RhB, 0.15g of synthesized ZnO NPs photocatalyst was added in 10 ppm solution of RhB under constant stirring. Prior to UV illumination, the suspension was continuously stirred for about 1h to develop adsorption–desorption equilibrium between RhB dye and photocatalyst under dark condition. Then, the stable aqueous dye solution was exposed to UV light illumination under constant stirring. The decomposed dye sample was periodically withdrawn after every 10 min and subjected to centrifuge at 12,000 rpm to separate out ZnO powder. Finally, the absorption spectrum of decomposed dye was collected using UV-Visible spectrophotometer (2550-Shimadzu, Japan). The degradation rate is calculated by following equation;

\[
\text{Photodegradation rate} = \left( \frac{C_0-C}{C_0} \right) \times 100
\]

Where \(C_0\) is the initial concentration at time \(t = 0\) min and \(C\) is the concentration at time=\(t\). Moreover, photocatalytic degradation of RhB dye followed the pseudo-first order kinetics and rate constant was determined by following relation;

\[
\ln(C_0/C) = kt
\]

The \(k\) was calculated from graph between \(\ln(C_0/C)\) vs. time interval, where \(C_0\) and \(C\) denote the RhB dye concentration at time, \(t=0\) and \(t=t\) respectively.
4.2.(I).3. RESULTS AND DISCUSSION

The field emission scanning electron microscopic (FESEM, JEOL-JSM 7600F) images of ZnO NPs are shown in Figure 4.2.(I).1. The synthesized ZnO nanostructures possess highly uniform spherical particles with the average diameter of 30-50 nm. Noticeably, most of the nanoparticles are uniform in size along with few big particles. The detailed morphology of ZnO NPs is further characterized by TEM and HRTEM, as shown in Figure 4.2.(I).2(a & b). The TEM image of synthesized ZnO NPs depicts the similar morphology of the FESEM micrographs in terms of its morphology and dimensions. It again deduces the uniform spherical particles with the average sizes of 30-50 nm. From the HRTEM image (Figure 4.2.(I).2.(b)), the distance between two parallel lattice fringes are ~0.52 nm, which is consistent with (001) crystal plane of wurtzite phase of ZnO. The corresponding SAED patterns reveal the typical wurtzite single crystalline structure which affirms the preferential growth oriented along c axis direction (001). From FESEM and TEM, the synthesized ZnO NPs exhibit nanograins form and contain the highly developed free surfaces and grain boundaries. As reported in literature, it has been demonstrated recently that the physical properties of nanograin ZnO strongly depend on the presence of defects like grain boundaries and the amorphous intergranular layers. Straumal et al. reported that the defects or grain boundaries of nanograins are defined ferromagnetic properties of ZnO NPs.
Figure 4.2. (I).1. FE-SEM image of ZnO nanoparticles.
Figure 4.2.(I).2. TEM (a) and HRTEM (b) images of ZnO nanoparticles. Inset shows the corresponding SAED patterns.

Figure 4.2.(I).3 shows the X-ray diffraction (XRD, Rigaku, operating at 40kV and 20mA using Cu Kα radiations, λ = 1.54171Å with scanning rate 4°/min) patterns of ZnO NPs. The XRD pattern of ZnO NPs are well indexed with JCPDS card No. 36–1451, suggesting the typical hexagonal wurtzite phase with the lattice parameters: a=3.246 and c=5.206Å. The average particle size of ZnO NPs was also estimated by the Debye-Scherrer equation:

$$D = \frac{K \lambda}{\beta \cos \theta},$$  \hspace{1cm} (4.2. (I).3)

Where, D is the mean particle size, K is a constant (0.94), λ is the wavelength (Cu-Kα = 1.54171Å), θ is the Bragg angle and β the full width at half maxima (FWHM) of a diffracted peak. By taking the FWHM at (101), the average particle size is found to be ~28 nm, which is consistent with FESEM and TEM results.

The optical properties of ZnO NPs have been studied by UV-Vis diffused
reflectance spectroscopy (Perkin Elmer Lambda-35), as shown in Figure 4.2.(I).4. The band gap energy of synthesized ZnO can be calculated from the optical absorption edge onset (λ) of reflectance spectrum by equation: E (eV) = 1240/λ (nm), Where λ is absorption edge and E is band gap energy of synthesized sample. ZnO NPs obtain a steep absorption edge lying between 370-390 nm, which corresponds to the wurtzite hexagonal phase of ZnO. The band gap energy is calculated as 3.29 eV (inset of Figure 4.2.(I).4) which is consistent with the band gap energy of bulk ZnO. Additionally, no other transition is observed in the spectrum which further confirms purity of synthesized ZnO NPs.

Figure 4.2.(I).3. XRD pattern of ZnO nanoparticles.
The textural properties i.e.; surface area, pore diameter and pore volumes were evaluated from nitrogen physisorption studies of ZnO nanoparticles. As shown in figure 4.2.(I).5, the ZnO nanoparticles exhibited type IV isotherm with distinct hysteresis loops observed in the range of 0.75-1.0 \( P/P_0 \). The pore diameter and surface area was found to be 10.285 nm and 7.8703 m\(^2\)g\(^{-1}\) from BET plot.

**Figure 4.2.(I).5.** BET surface area plot of ZnO nanoparticles.
The growth of ZnO NPs can be explored by considering the involved chemical reactions in the synthesis process. Herein, no immediate precipitation or colorless solution was seen by the mixing of aqueous solutions of zinc acetate and oxalic acid. The sequential reactions are as follows:

\[
\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Zn(}_\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O} + 2\text{CH}_3\text{COOH} + 2\text{H}_2\text{O}
\]

\((4.2.4\).I.4)
The formation of zinc oxalate complex, Zn(C₂O₄)·2H₂O is important primary step for growth of wurtzite ZnO crystal, which acts as a building block for synthesis of ZnO NPs. The Zn(C₂O₄)·2H₂O complex has been further calcined at 400°C for 30 min. to convert Zn(C₂O₄).2H₂O into pure ZnO crystals.

\[
\text{Zn(C₂O₄)·2H₂O + \frac{1}{2} O₂ → ZnO + 2CO₂ + 2H₂O} \quad (4.2. (I).5)
\]

Hence, the described reactions explain the proper growth of wurtzite ZnO. Therefore, it is expected that electrostatic attraction of oxalate ligand also play pivotal role in the uniform nucleation for ZnO growth.

The RhB dye degradation was demonstrated over the surface of ZnO NPs under UV illumination to elucidate the photocatalytic activity. Figure 4.2.(I).6(a) shows UV-Vis spectra of decomposed RhB dye with the variation of time from 0-70min and exhibits the maximum absorption wavelength at ~554nm. The absorbance intensities of RhB are gradually decreased in the presence of ZnO NPs with the increase of exposed time, indicating the decrease in RhB dye concentrations. RhB dye significantly degrades by ~95% within very short exposed time (70min). However, the RhB dye color/concentration is not changed when reaction was performed under dark for 1-2 h. Figure 4.2.(I).6(b) shows the degree of RhB dye degradation in the presence of ZnO NPs as a function of time under UV illumination. The relative concentration of RhB dye decreases with the increase of exposed time. Furthermore, the pie chart of RhB dye degradation (Figure 4.2.(I).7(b)) reveals that most of dyes are degraded in the first 30 min. over the surface of ZnO NPs, suggesting the fast RhB dye degradation under UV-Illumination.

The kinetics of RhB degradation reaction is represented in Figure 4.2.(I).7(a), which follows apparent first order kinetics in agreement with a general Langmuir – Hinshelwood mechanism;
\[ r = - \frac{dC}{dt} = \frac{kKC}{1+KC} \]  
\[ (4.2.(I).6) \]

Where, \( r \) is the degradation rate of reactant (mg/l min), \( C \) is the concentration of reactant (mg/l), \( t \) is the illumination time, \( K \) is the adsorption coefficient of reactant (l/mg) and \( k \) is the reaction rate constant (mg/l min). If \( C \) is very small then the above equation could be simplified into:

\[ \ln \left( \frac{C_0}{C} \right) = k K t \approx k_{app} t \]  
\[ (4.2.(I).7) \]

A plot between \( \ln(C_0/C) \) vs time represents a straight line, the slope is equal to the apparent first order rate constant \( k_{app} \) (0.0343 min\(^{-1}\)). This result is also in consistence with previously reported works for RhB degradation by other catalyst.\(^{18}\) Figure 4.2.(I).8 depicts the plausible schematic illustration for RhB dye degradation over ZnO NPs. Upon illumination, the generation of electron-hole (e\(^-\) h\(^+\)) pairs between in conduction (CB) and valence band (VB) of ZnO NPs with high surface area (7.8703 m\(^2\)g\(^{-1}\)) is generally responsible for degrading RhB dye.\(^{19}\) First, the photogenerated e\(^-\) in CB ZnO moves towards the surface and scavenges by the ubiquitously O\(_2\) to generate super oxide anion O\(_2\)\(^-\), simultaneous protonation yields HOO\(^-\) radicals. While h\(^+\) in VB migrates to the back side of the ZnO surface and reacts with either H\(_2\)O or OH\(^-\) to produce an active species such as OH\(^-\). These processes might be attributed to the efficient separation of photogenerated e\(^-\) h\(^+\) pairs which effectively play a pivotal role in RhB degradation. The following steps are possible in the degradation of RhB\(^{20}\):

\[ \text{ZnO} + h\nu \rightarrow e^{-}_{\text{cb}} + h^{+}_{\text{vb}} \]  
\[ (4.2.(I).8) \]

\[ O_2 + e^{-} \rightarrow O_2^{-} + H^{+} \rightarrow \text{HOO}^{-} \]  
\[ (4.2.(I).9) \]

\[ e^{-} + \text{HOO}^{-} + H^{+} \rightarrow H_2O_2 \]
\[ \text{(4.2.(I).10)} \]

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^+ + \cdot\text{OH} \]

\[ \text{(4.2.(I).11)} \]

\[ \text{RhB} + \{\text{O}_2, \text{O}_2^-, \text{HOO}^-, \text{or} \cdot\text{OH}\} \rightarrow \text{Peroxy or hydroxylate intermediate} \rightarrow \text{Mineralized product} \]

From the above reactions, the active oxygen species \{\text{O}_2, \text{O}_2^-, \text{HOO}^-, \text{or} \cdot\text{OH}\} are responsible for degradation of RhB dye into less harmful materials and minerals. Additionally, the amorphous intergranular layers are seen at the boundaries of ZnO nanograins, as shown in TEM image, which is evidence of the generation of free surfaces and higher density of grain boundaries in the larger particles due to presence of high density of defects. This behavior might produce the large number of active sites and facilitate the fast photocatalytic degradation of RhB dye. Thus, well crystalline, and good optical properties of ZnO NPs with higher density of grain boundaries substantially increase the reactive species over the surface of catalysts, resulting in the fast degradation of RhB dye under UV illumination.

**Figure 4.2.(I).6.** (a) UV-Vis absorbance spectra of RhB dye as function of time over ZnO nanoparticles under UV illumination and (b) Extent of degradation of RhB dye in every successive time interval.
Figure 4.2.(I).7. (a) Kinetics of RhB dye degradation for first order linear plot $\ln C_0/C = f(t)$ and (b) RhB dye degradation pie chart as a function of time.

Figure 4.2.(I).8. A schematic diagram of RhB degradation reaction mechanism over the surface of ZnO nanoparticles.
4.2.(I).4. CONCLUSION

The highly crystalline ZnO NPs were synthesized by solution phase approach with zinc acetate as precursor and oxalic acid at 80°C. The ZnO NPs were characterized in terms of morphological, structural, optical properties by FESEM, TEM, HRTEM, XRD and UV-DRS techniques, respectively. The synthesized ZnO NPs exhibited monodispersity with the average size 20-30 nm. The photocatalytic activity was carried out by performing the decomposition of RhB dye under UV illumination over as-synthesized ZnO NPs. RhB dye considerably degraded by ~95% within 70min over the ZnO NPs. The rate constant for the dye degradation reaction was found to be k= 0.0343 min⁻¹ which has followed the 1st order kinetic mechanism.
4.2.(II) Structural, Optical and Photocatalytic Properties of Hexagonal ZnO Nanorods Assembled in Flower-Shaped Morphologies

4.2.(II).1. INTRODUCTION

Industrial development is pervasively connected with the disposal of a large number of various toxic pollutants that are not only harmful to the environment, but also hazardous to human health, and difficult to degrade by natural means.\(^{21}\)

To overcome such serious environmental problems, people have started doing intense research in the field of “green chemistry”. Semiconductor photo-catalysis is among the most promising technology for green earth and renewable energy. The application of semiconductor photocatalysis in the field of science and engineering is an emerging area of research with the industrial development.\(^{22, 23}\)

Since, the work of Fujishima and Honda on photocatalytic splitting of water in 1971 using TiO\(_2\) semiconductor, which opened a new door for efficient utilization of solar energy in photo-catalytic degradation of non-biodegradable dyes.\(^{24}\) Among the various known techniques, heterogeneous photo-catalysis is the most widely employed process to eliminate hazardous waste materials especially organic compounds. Application of semiconductor photo-catalysts, potentially toxic organic compounds can be efficiently degraded into carbon dioxide and water molecules or less harmful materials.

Due to presence of some exotic and fascinating properties of II-VI wurtzite hexagonal phase ZnO, it requires special attention among the various metal oxides. The splendid characteristic properties of ZnO includes wide band gap (3.37eV), high-excitation binding energy (60 meV), semiconducting nature, high thermo-mechanical stability, piezoelectric and optoelectric properties.\(^{6}\) These fascinating properties make ZnO one of most important multifunctional materials that is being used in fabrication of light emitting diodes (LEDs), laser diodes, surface acoustic wave filter, photonic crystal, photodetector, optical modular and so forth. It is also
an attractive material for fabrication of solar cells, chemical sensor, hydrogen storage and so forth.

Among various available oxide semiconductor photocatalytic materials, TiO₂ and ZnO draw special attention of physicists, chemists and material scientists because of their photosensitive nature, non-toxicity, biocompatibility and wide band gap. TiO₂ based photocatalysis have been widely used for photodegradation of dyes, but ZnO has become one of the most important and alternative material for photocatalysis due to its own properties and having similarities with TiO₂. Interestingly, it has been reported that ZnO absorbs more fraction of solar spectrum than TiO₂. The ZnO nanostructure crystals enable various morphological features such as nanorods, nanobelts, nanotubes, nanosprings and nanospirals, polyhedral cages, porous webby, sea urchin and comb like and other complicated morphologies, which is not possible in case of TiO₂. Recently, ZnO nanomaterials as a photocatalyst have received a wide attention in research because of its impressive catalytic activity and quantum efficiency compared to that of widely used TiO₂ nanomaterials.

So far, various ZnO nanostructures have been used to degrade the harmful dyes into less harmful components by photocatalytic reaction under UV light illumination. Recently, H. Usni has reported the surfactant assisted chemical synthesis of ZnO nanorods and they used as-synthesized ZnO nanorods as photocatalyst for efficient degradation of MB dye. They have also shown a ~90% degradation of MB in 7 hours. Yu J. and Yu X. reported the hydrothermal synthesis of zinc oxide hollow spheres and they have shown facile degradation of Rhodamine-B in 4 hours in the presence of UV light illumination over ZnO. Zhang K. and Oh W-C. reported a facile degradation of three dyes; Methylene Blue, Rhodamine-B and Methylene Orange over activated carbon composite of TiO₂ and they have shown successfully that the rate of degradation of MB is faster
than other two dyes.\textsuperscript{39} In a similar work, Comparelli \textit{et al.} have studied photo degradation of two organic dyes; Methyl Red and Methyl Orange over TiO\textsubscript{2} mediated reaction under UV light illumination. Experiments taken under best reaction conditions and it were observed that the degradation of Methyl Red was much faster as compared to Methyl Orange over TiO\textsubscript{2}.\textsuperscript{40} Recently; Zhang \textit{et al.} synthesized porous ZnO spheres using soluble starch-assisted method and demonstrated its photocatalytic activity over RhB and 4-nitrophenol.\textsuperscript{41}

Herein, an effective cationic surfactant cetyltrimethylammonium bromide (CTAB) assisted hydrothermal method for facile synthesis of hexagonal shaped ZnO nanorods was used. The photocatalytic properties of as-synthesized ZnO nanorods were executed in study of degradation of organic dyes; Methylene Blue (MB) and Rhodamine-B (RhB) under UV light illumination. While keeping all the discoloration reaction parameters same, kinetics of discoloration of organic dyes; MB and RhB is also studied.

\textbf{4.2.(II).2. EXPERIMENTAL}

For the facile synthesis of ZnO nanorods assembled into flower shaped morphology, analytical grade zinc acetate (Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O, 99.8\%), hexamethylenetetramine (HMTA, C\textsubscript{6}H\textsubscript{12}N\textsubscript{4}, 99.8\%), sodium hydroxide (NaOH) and cetyltrimethylammonium bromide (CTAB) were procured from Sigma-Aldrich and were used without further purification. In a typical procedure, 0.05M zinc acetate solution, 0.05M hexamethylenetetramine solution and 1M sodium hydroxide solution were prepared in deionized water under continuous stirring at ambient temperature in separate beakers. First, Hexamethylenetetramine (HMTA) solution was gradually added into zinc acetate solution with constant stirring followed by drop-wise addition of sodium hydroxide solution to maintain the pH \textasciitilde11-12. The above solution was further stirred for 30 minutes. The resulting
solution was gradually added into the cetyltrimethylammonium bromide solution. After 30 minutes of vigorous stirring the obtained solution was transferred into a 250 mL Teflon-lined stainless steel autoclave and heated up to 105 ±5 °C for 10 hours. Now, the autoclave was allowed to cool gradually to the room temperature. White crystalline powder was obtained which was washed repeatedly with deionized water followed by ethanol and acetone and dried in oven at 50 °C for 30 minutes.

The structural properties of as-synthesized ZnO nanorods assemble into flower shaped were examined by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and high resolution TEM (HRTEM) equipped with selected area electron diffraction (SAED) pattern. The crystal phase and crystallinity were analyzed by powder X-ray diffraction (PXRD) with Cu Kα radiations \( \lambda = 1.54178 \) Å with 4°/min scanning rate in the range of 20-80°.

The chemical composition was analyzed by using energy dispersive spectroscopy (EDX) attached with FESEM. The quality and composition were examined by Fourier transform infrared spectroscopy in the range of 400-4000 cm\(^{-1}\). The optical property as-prepared ZnO nanorods were analyzed by UV-Visible absorption spectroscopy at ambient temperature.

The photocatalytic activities of as-synthesized ZnO nanorods assemble into flower shaped were measured by monitoring the decompositions of organic dyes; MB and RhB. The photocatalytic reaction was executed in Pyrex flask type reactor under the illumination by using xenon arc lamp (Thoshiba, SHLS-1002) at ambient temperature to about 28°C. The efficiency of photocatalytic activities was studied by monitoring the changes in absorbance spectra of the basic organic dyes; MB and RhB in an aqueous solution containing ZnO nanorods photocatalyst under constant stirring and also provided with continuous exposure of UV-light irradiation.
For the effective degradation of organic dyes such as MB and RhB, an appropriate amount of dyes were dissolved in 100 mL water to get the concentration of 10 ppm and disperse 0.15g of as-synthesized ZnO photocatalyst under constant stirring. Prior to illumination, suspension was continuously stirred for about 1 hour to develop adsorption–desorption equilibrium between dye and photocatalyst in the dark. After that oxygen is commonly provided to stable aqueous suspension in order to scavenge electron from the catalyst surface. Then, the stable aqueous dye suspension was exposed to UV light illumination under constant stirring. The sample was periodically and successively taken out from Pyrex reactor after every 10 minutes of time interval and subjected to centrifuge at 12,000 rpm to filter out ZnO powder, and then an absorption spectrum of decomposed dye solution was measured using UV-visible spectrophotometer. Moreover, the photo-catalytic degradation of dye followed the pseudo-first order kinetics and rate constant was determined by following relation;

\[ \ln(C_0/C) = kt \]  

(4.2.(II).1)

The k was calculated from graph between \( \ln(C_0/C) \) vs time interval, where \( C_0 \) and \( C \) denote the dye concentration at time, \( t=0 \) and \( t = t \) respectively.

4.2.(II).3. RESULTS AND DISCUSSION

4.2.(II).3.1. Structural and Optical properties of as-synthesized hexagonal shaped ZnO Nanorods

The general morphologies of as-synthesized ZnO nanorods assemble into flower shaped morphology were examined by field emission scanning electron microscopy (FESEM, JEOL-JSM 7600F) and electron micrographs were depicted in Figure 4.2.(II).1. As shown in figure 4.2.(II).1(a), the low magnification FESEM image confirm the uniform and dense growth of perfectly hexagonal shaped ZnO
nanorods. Interestingly, it is seen that hexagonal ZnO nanorods are assembled into flower like bunches and each bunch is composed of several hundred hexagonal ZnO nanorods. In figure 4.2.(II).1(b), we have shown the high-magnification image as well as typical length of as-synthesized perfectly hexagonal shaped ZnO nanorods. The diameter of the ZnO nanorods lies in the range of 250 ± 20 nm. Moreover, it is interesting to observe that the hexagonal ZnO nanorods were tapering at their end and exhibited a perfectly hexagonal, clean and smooth surface throughout their lengths. It is also obvious from the micrographs that each ZnO nanorod is constituted of six crystallographic planes, where each plane connected by a 60° internal angle.

The crystallinity and crystal phase of as-synthesized perfectly hexagonal shaped ZnO nanorods were analyzed by powder X-ray diffraction (PXRD, Rigaku, operating at 40 kV and 20 mA using Cu Kα radiations, λ=1.54171 Å with scanning rate 4°/min) pattern and shown in figure 4.2.(II).2(a). The major reflections were appeared at 32.41°, 35.19°, 36.96°, 48.25°, 57.28°, and 63.41°correspondes to lattice planes of (1010), (0002), (1011), (1012), (1120), and (1013) respectively. All the diffracted peaks in PXRD pattern were fully matched with pure wurtzite phase of ZnO crystals and equates with JCPDS (Joint committee on Powder Diffraction Standard) card number 36-1451. No other peaks were detected in PXRD pattern within the detection limit of X-ray diffraction, conforming that the as-synthesized nanorods are made up of pure ZnO and possess wurtzite phase.

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To investigate the chemical composition of as-synthesized hexagonal ZnO nanorods, energy dispersive X-ray (EDX) spectroscopy has been performed and shown in figure 4.2.(II).2(b). The observed elemental compositions are in full agreement with calculated stoichiometric value of zinc and oxygen in ZnO nanorods. Since the absence of any stray peaks in EDX spectrum except zinc and oxygen atoms confirmed that the as-synthesized hexagonal ZnO nanorods are made up of only zinc and oxygen. Therefore, both PXRD pattern and EDX spectra clearly indicate that the as-synthesized hexagonal ZnO nanorods are constituted of zinc and oxygen atoms only.
The detailed structural characterizations of as-synthesized hexagonal ZnO nanorods were studied by the transmission electron microscopy (TEM). For TEM analysis, the as-synthesized ZnO nanorods were dispersed into acetone and a few drops of acetone containing ZnO nanorods poured on the TEM grid and examined. Figure 4.2.(II).3(a) depicts low magnification TEM image of as-synthesized ZnO nanorods which exhibited full consistency with FESEM results in terms of their morphology and dimensions. It is observed that the as-synthesized hexagonal ZnO nanorods were tapering towards their end and possessing the typical diameter about 250 nm which was fully corroborated with FESEM results. The HR-TEM image of ZnO nanorods are depicted in figure 4.2.(II).3(b); it clearly exhibits the distance between two parallel lattice fringes is ~0.52 nm, which belongs to [0001] crystal plane of wurtzite phase of ZnO.\textsuperscript{42} The result of HRTEM revealed that the as-synthesized hexagonal ZnO nanorods are almost defect free and exhibited good crystallinity. The corresponding SAED pattern projected along [2110] zone axis is fully consistent with HRTEM observation and confirmed that as-grown hexagonal ZnO nanorods exhibited typical wurtzite single crystalline structure and affirm the preferential growth oriented along c axis [0001] (inset Figure 4.2.(II).3 b).
The quality and chemical composition of as-synthesized hexagonal ZnO nanorods were characterized by Fourier Transform infrared (FTIR) spectroscopy in the range of 400-4000 cm$^{-1}$ at ambient temperature and shown in figure 4.2.(II).4. Several absorption bands have been observed in the FTIR spectrum of hexagonal ZnO nanorods. The absorption reveals a strong absorption band at 561 cm$^{-1}$; which attributes the formation of wurtzite phase ZnO.$^{43}$ Moreover in ZnO spectrum, the appearance of a weak band at 862 cm$^{-1}$ can be attributed to presence of carbonate ion (CO$_3^{2-}$) which was unremarkably appear imputable when FT-IR measures in the air.$^{15}$ In addition to this, a small peak at 1424 cm$^{-1}$ was due to the stretching mode of vibration of C-O bond.
The optical properties of as-synthesized hexagonal shaped ZnO nanorods were measured by UV-visible absorption spectrum (PerkinElmer Model 750) at ambient temperature and result was depicted in the figure 4.2.(II).5. For this measurement, ZnO nanorods are well dispersed in water and absorbance of the dispersed ZnO-water solution was measured over the range of 300-700 nm. As can be seen, the obtained spectrum exhibited well distinct broad absorption peak at 374 nm, which is in a good agreement with the characteristic peak (368 nm) for wurtzite ZnO. Except from characteristic peak, there was no other peak throughout the spectrum which further support that the as-synthesized sample belongs to pure wurtzite ZnO.

Figure 4.2.(II).4. FTIR spectrum of synthesized ZnO nanorods
Figure 4.2.(II).5. UV-Vis spectrum of synthesized ZnO nanorods.
4.2.(II).3.2. Plausible growth mechanism of hexagonal shaped ZnO nanorods

The growth of as-synthesized ZnO nanorods assemble into flower shaped morphology can be explored by considering the involved reactions in the synthesis process. In the typical experimental procedure, the aqueous solution of hexamethylenetetramine (HMTA) gradually poured into zinc acetate solution, it is important to note that there was no immediate precipitation but the clear zinc acetate solution turned into turbid solution. Moreover, the pH of resulting solution was adjusted to ~11-12 by addition of few drops of sodium hydroxide solution. The gradual increase of temperature in the hydrothermal reactor would facilitate the thermal degradation of HMTA and subsequently release of hydroxyl ions which further react with Zn$^{2+}$ ions to form Zn(OH)$_2$.\(^{45}\) The sequential reactions are as follows:

\[
\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 + 2\text{CH}_3\text{COONa} + 2\text{H}_2\text{O} \\
\text{(4.2.(II).2)}
\]

\[
(\text{CH}_2\text{)}_6\text{N}_4 + 6\text{H}_2\text{O} \leftrightarrow 6\text{HCHO} + 4\text{NH}_3 \\
\text{(4.2.(II).3)}
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{(4.2.(II).4)}
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \leftrightarrow \text{Zn(OH)}_2 \\
\text{(4.2.(II).5)}
\]

In addition to this, the zinc hydroxide Zn(OH)$_2$ further reacts with hydroxyl ions to form Zn(OH)$_4^{2-}$:

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \text{(from NaOH)} \rightarrow \text{Zn(OH)}_4^{2-} \\
\text{(4.2.(II).6)}
\]

As the reaction takes place in the presence of cetyltrimethylammonium bromide solution at appropriate zinc acetate/CTAB ratio, the CTAB being a cationic surfactant reduces the surface tension and inhibits the formation of new phase.
CTAB plays two pivotal roles in the synthesis; first CTAB can effectively control the morphology of building blocks for the synthesis of hexagonal ZnO nanorods. It is well-known that the kinetics for morphological dynamics can be adjusted by using selective adsorption of surfactants.\textsuperscript{46} Second; CTAB facilitates molecular aggregation above Critical Micelle Concentration (CMC) producing spherical micelles at relatively low concentration. The CTAB also facilitates to transport of Zn(OH)$_4^{2-}$ growth units which come together to form individual rod-like structures. These rod-like structures further self-assemble into flower like morphology. As the reaction aged at 105°C for 10 hours, Zn(OH)$_4^{2-}$ ions dissociate to form ZnO nuclei as follow;

$$\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^-$$

(4.2.(II).7)

The formation of flower like assembly of ZnO proceed by two step mechanism in aqueous solution, First nucleation followed by growth of nanorods around these nuclei and plausible mechanism has shown in fig. 4.2.(II).6. The ZnO is polar crystal in which O$^{2-}$ ions are in hexagonal close packing and Zn$^{2+}$ ions lie in the tetrahedral hole of four oxygen ions. The Zn and O atoms are arranged alternatively along the c-axis and top surface-plane is Zn terminated (0001), which is catalytically active while the bottom surface is O terminated (000$\bar{1}$), which is chemically inert.\textsuperscript{47} The morphology of nanostructures is greatly affected by the growth velocity of ZnO into the different directions. According to the Laudise \textit{et al.}, the growth velocities of ZnO crystal in the different planes are [0001] > [00 $\bar{1}$ $\bar{1}$] > [01$\bar{1}$ 0] > [01 $\bar{1}$ 1] > [000 $\bar{1}$], under the hydrothermal conditions.\textsuperscript{48} According to the ideal growth rates in different crystal plane, the growth along (0001) plane is maximum and as-synthesized nanorods contains ± (0001) crystal plane at their top and bottom and however, enclosed by the six equivalent (01$\bar{1}$0) crystal planes.\textsuperscript{49} It
is well known that the fastest growing planes generally disappear earlier and leaving behind the slower growing forms with lower energy. Hence, the (0001) plane will not be in equilibrium with other growing planes. As the specific surface energy, free energy of the (0001) plane are higher than other growing planes, hence after the synthesis, (01 \bar{1} 1) plane would remain with ZnO crystal. Hence, due to electrostatic interaction between ions and polar surface, there would be formation of hexagonal ZnO nanorods assembled into flower like morphology. The as-synthesized product was further calcined at 400 °C for about 30 minutes; heating will facilitate the decomposition of organic moiety and improve the crystallinity via eliminating additive from inter-crystal free space.\textsuperscript{50} Interestingly, it is observed that the as-synthesized ZnO nanorods follow the same growth pattern as reported in the literature for ideal growth of hexagonal wurtzite ZnO crystals.\textsuperscript{51}
Figure 4.2.(II).6. Plausible growth mechanism of hexagonal-shaped ZnO nanorods assembled into flower like morphology.
4.2.(II).3.3. Photocatalytic decomposition of Organic Dyes; Methylene Blue and Rhodamine-B using as-grown hexagonal–shaped ZnO nanorods
The photocatalytic activity of as-synthesized hexagonal shaped ZnO nanorods assembled in the flower like morphology was effectively demonstrated over efficient degradation of organic dyes; MB and RhB. The chemical structure of organic dyes has played substantial impact on dye degradation reaction over semiconductor photocatalyst under UV light illumination. The photocatalytic decompositions of MB and RhB dyes was studied by monitoring the changes in their characteristic absorption under UV light illumination and rate of degradation reaction is estimated by observing the changes in absorbance (decrease in absorption intensity vs. irradiation time) obtained by UV-Vis spectra.

In Figure 4.2.(II).7(a) we have shown the typical time dependent UV-Vis absorption spectrum of MB dye in the presence of hexagonal shaped ZnO nanorods as a photocatalyst under UV light illumination. The MB exhibited $\lambda_{\text{max}}$ at 661nm; the intensity of the absorption band diminishes chronologically with respect to time. Figure 4.2.(II).7(a) shows temporal changes of MB dye with variation of time from 0-140 minutes and absorption wavelength in the range 480-800 nm. The absorption intensity gradually decreases at 661nm as shown in Figure 4.2.(II).7(a). While the figure 4.2.(II).7(b) depicted the time dependent UV-Vis absorption spectral changes of aqueous RhB dye suspension in the presence of hexagonal shaped ZnO nanorods as a photocatalyst under UV-light illumination. It was important to note that the RhB follows two competitive degradation pathways; either de-ethylation or cleavage of chromophore ring structure. Furthermore, the primary characteristic absorption peak of RhB i.e., $\lambda_{\text{max}}$ at 554nm did not shift during the dye decomposition under illumination, which could possibly be due to the degradation of RhB which proceeds through $'OH$ radical attacks on the aromatic ring rather than de-ethylating RhB.20 The characteristic absorption peak of RhB i.e., $\lambda_{\text{max}}$ at 554 nm decreases gradually with variation of time from 0-140 minutes which is depicted in Figure 4.2.(II).7(b).
Figure 4.2.(II).7. Distinctive discoloration Mechanism, (a) The UV-Vis absorbance spectrum of MB dye solution as function of time upon UV illumination over ZnO nanorods and (b) The UV-Vis absorbance spectrum of RhB dye solution as function of time upon UV illumination over ZnO nanorods.

Figures 4.2. (II).8(a) and 4.2.(II).9(a) exhibited the typical time dependent photodegradation reaction efficiency as a function of irradiation time interval in the presence and absence of hexagonal shaped ZnO nanorods assembled in the flower
like morphology of MB and RhB dye respectively. The relative concentration of MB and RhB dye decreases with the increase of exposed time.

The extent of dye degradation reaction mediated over the surface of ZnO nanorods is calculated by the following relation;

\[
\text{Extent of degradation} \, (\%) = \frac{(C_o - C)}{C_o} \times 100 = \frac{(A_o - A)}{A_o} \times 100
\]

(4.2.(II).8)

Where \(C_o\) represents the initial concentration at time \(t=0\), while \(C\) denotes the concentration at time \(t\), and \(A_o\) shows initial absorbance and \(A\) corresponds to absorbance at time \(t\) respectively.

It is noteworthy that there was no appreciable degradation occurred under UV light illumination in the absence of photocatalyst. While in the presence of ZnO nanorods acting as a photocatalyst, it was estimated that about 91% MB is degraded within just 140 minutes of time span under UV-light illumination. It was observed that during first 60 minutes of time interval, the extent of degradation was very fast and almost 60% degradation occurred and after that very slow degradation was observed as depicted in pie chart of MB degradation reaction in figure 4.2.(II).8(b). Furthermore, the pie chart for RhB degradation as shown in Figure 4.2.(II).9(b), it is noteworthy to mention that the degradation rate was accelerative in successive way and almost 80% degradation has been accomplished within 140 minutes time of illumination. This suggests that the as-synthesized hexagonal shaped ZnO nanorods work as good photocatalyst.

**Figure 4.2.(II).8.** (a) Extent of discoloration of MB dye in every successive time interval and (b) MB discoloration pie chart as function of time.
Figure 4.2.(II).9. (a) Extent of discoloration of RhB dye in every successive time interval, and (b) RhB dye discoloration pie chart as function of time.
The kinetics of organic dyes; MB and RhB degradation reaction is represented in fig.4.2.(II).10. The dyes follow apparent first order kinetics which is in good agreement with a general Langmuir–Hinshelwood mechanism;

\[
    r = - \frac{dC}{dt} = \frac{kKC}{1+KC}
\]

(4.2.(II).9)

Where, \( r \) is the degradation rate of reactant (mg/1 min), \( C \) is the concentration of reactant (mg/l), \( t \) is the illumination time, \( K \) is the adsorption coefficient of reactant (l/mg) and \( k \) is the reaction rate constant (mg/l min). If \( C \) is very small then the above equation could be simplified into;

\[
    \ln\left(\frac{C_0}{C}\right) = kKt \approx k_{app} t
\]

(4.2.(II).10)

The plots between \( \ln(C_0/C) \) vs. time represents a straight line, the slope is equal to the apparent first order rate constant and calculated value of rate constant was \( k_{app} \) (0.01313 min\(^{-1}\)) and \( k_{app}(0.0104 \text{ min}^{-1}) \) for MB and RhB dye respectively. This result is also in consistence with previously reported works for MB and RhB degradation by other catalysts.\(^{52,53}\)
Figure 4.2.(II).10. Kinetics study of dye discoloration (a) MB and (b) RhB, exhibited typical First order liner plot \( \ln C_0/C = f(t) \).
In the view of aforementioned outcomes, we propose the plausible schematic illustration for dye degradation over ZnO nanorods under UV light illumination which is shown in figure 4.2.(II).11. Upon illumination, there is generation of electron and hole pairs in the conduction band and valence band respectively. Interestingly, the adsorbed oxygen play a pivotal role in the dye degradation reaction by combining with electron (e⁻) in conduction band and generate superoxide radical anion O₂⁻, instantaneously superoxide radical anion (O₂⁻) get protonated to yield HOO’ radicals otherwise if there is no available oxygen then it might be possible that electron and hole pairs again recombined and diminishes reaction efficiency. Whereas, photo generated hole h⁺ in VB react with either H₂O/OH⁻ and dye molecules to generate an active species such as OH’ and dye⁺. The following steps could be possible in the dye degradation reaction mediated over ZnO semiconductor upon illumination of light;

(i) Photoexcitation:

\[ \text{ZnO} + h\nu \rightarrow e^- \text{(conduction band)} + h^+ \text{(valence band)} \quad (4.2.(II).11) \]

(ii) Oxygen ionosorption:

\[ O_2 + e^- \rightarrow O_2^- + H^+ \rightarrow \text{HOO'} \quad (4.2.(II).12) \]

(iii) Ionizations of water:

\[ \text{H}_2\text{O} + h^+ \rightarrow \cdot\text{OH} + \text{H}^+ \quad (4.2.(II).13) \]

(iv) The hydroxyl radical formed in the step (ii) also has scavenging property as O₂ thus doubly prolonging the lifetime of photon hole

\[ e^- + \text{HOO'} + H^+ \rightarrow \text{H}_2\text{O}_2 \]
It was worthy to denote that the as-synthesized hexagonal shaped ZnO nanorods were assembled in the flower like morphology exhibits excellent photocatalytic properties and leads to facile degradation of organic dyes; MB and RhB about 91% and 80% within just 140 minutes. Figure 4.2.(II)12 depicts the histogram of extent of degradation reaction of MB and RhB as a function of illumination time. It is interesting to write that degradation of MB is much easier as compared to RhB in same span of time and that could be attributed due to difference in their chemical structure. The structure of MB is simple compared to RhB that might be the reason for their rate of discoloration. This result is further supported from the previous reported results.

Since the photocatalytic reaction mediated on the semiconductor surface, hence by providing superior electron mobility i.e., suppressing the recombination of electron and hole and a larger surface area such that more dye molecules can be adsorbed which would facilitate photocatalytic reaction.² ⁵⁴ The crystalline nature of as-synthesized hexagonal shaped ZnO nanorods greatly affects their photocatalytic activity. Amorphous ZnO photocatalyst seldom display photocatalytic activity due
to the presence of non-bridging oxygen atom in the bulk ZnO, which alter the proper stoichiometric arrangement of Zn-O in the lattice plane. That will facilitate the recombination of electron and hole and diminishes degradation reaction efficiency.\textsuperscript{54, 55}

Hence, the aforementioned results argue that the as synthesized hexagonal shaped ZnO nanorods were assembled in the flower like morphology were exhibited good crystal quality which could fully facilitate dye degradation reaction mediated over ZnO nanorods as an excellent photocatalyst.

**Figure 4.2.(II).11.** A schematic illustration for basic mechanism of degradation reaction mediated over the surface of ZnO nanorods upon UV illumination
Figure 4.2.(II).12. Histogram for comparative extent of discoloration of MB and RhB as function of time
4.2.(II).4. CONCLUSION

In summary, the well-crystalline hexagonal shaped ZnO nanorods were assembled in the flower like morphology has been successfully synthesized by facile CTAB-assisted hydrothermal process followed by calcinations. The as-synthesized hexagonal shaped ZnO nanorods were characterized in terms of their morphological, structural and optical properties by various analytical techniques which confirm that the as-synthesized products are pure ZnO, possessing well crystalline wurtzite hexagonal phase and exhibiting good optical properties. The possible growth mechanism and reactions involved have been discussed in details. To evaluate photocatalytic activity of as-synthesized hexagonal shaped ZnO nanorods, photodegradation reaction of organic dyes; MB and RhB has been studied, which exhibits sufficiently high degradation ~91% and ~80% within 140 minutes for MB and RhB respectively. The degradation of MB and RhB followed 1\textsuperscript{st} order kinetic mechanism and rate constants were determined $k_{\text{app}}$ (0.01313 min\textsuperscript{-1}) and $k_{\text{app}}$ (0.0104 min\textsuperscript{-1}) respectively. The obtained results argue that the as-synthesized hexagonal shaped ZnO nanorods can efficiently utilized for the effective photocatalytic degradation of organic dyes.
References


4.3. CuO nanomaterials: Growth and Properties

“Growth and structural properties at low temperature synthesis of 1-D CuO nanostructures”

4.3.1. INTRODUCTION

In the recent years, design and development of large scale self-assembly of meso, micro and nanostructure semiconductor assemblies have drawn significant interest because of their application in the development of economically viable solar cells, and also as a potential candidate in the field of photocatalytic system.1-5 A large number of 1D nanostructures have been synthesized over past decade. One dimensional nanobuilding blocks of transition metals oxides, hydroxides, sulfides, have been prepared via various techniques .6, 7

CuO is an important p-type transition metal-oxide semiconductor, with a narrow band gap (E_g =1.2eV) and exhibiting a versatile range of applications such as fabrication of electrical, optical, photovoltaic devices 8, 9, gas sensing 10, 11, heterogeneous catalysis 12, and magnetic storage media. In addition, CuO is potentially useful component in the fabrication of solar cells, lithium ion electrode materials and photothermal and photoconductive applications 13 and so forth. It
also reveals complex magnetic phase and, thus form basis for several high
temperature superconductors and materials with high magnetoresistance. 14, 15
Moreover, it can be used to prepare a variety of organic–inorganic nanostructure
composite with unique characteristics, which includes high thermal and electrical
conductivities, high mechanical strength, and high temperature durability and so
on. Because of versatile properties and wide applications in various fields, the
synthesis of nanostructure CuO has shown a potential need, however various kind
of nanostructure CuO have been synthesized by using different techniques, which
includes hydrothermal,16 sol-gel, 17 gas-phase oxidation, micro emulsion and so
forth. Usually the solution process is an easy and cost effective approach to obtain
nanostructures with appreciable yield. Therefore, various classes of CuO
nanostructures such as nanoparticles (zero dimensions), nanorods, nanowires,
nanoribbons have been reported in literature. Recently, Wang et al. have reported
1D CuO nanowhiskers using copper chloride, sodium hydroxide and ethylene
glycol through wet chemical reaction method at relatively low temperature.18 In
addition to low temperature pathway, Wu and coworkers have synthesized CuO
nanotube through template method at elevated temperature of 450-750 °C. 19 On
the other hand Xu et al. have reported CuO nanoparticles (zero dimensions) by
thermal deposition of copper acetate at 950 °C. 20 Until now, there have been many
papers based on the solution process reported in the literature. But there is still
work need to be done to reach at general conclusion.

Herein, a facile and simple method was used for synthesis and characterization of
highly crystalline and elongated CuO microstructures at low temperature.
Moreover, several experiments have been carried out to propose the growth
mechanism of highly oriented and crystalline CuO microstructures.
4.3.2. EXPERIMENTAL
All the chemicals were analytical grade and used as without further purification. The typical reaction process for the synthesis of CuO microrods copper acetate Cu(CH₃COO)₂.2H₂O (99.8% Sigma-Aldrich), Hexamethylenetetramine (HMTA; C₆H₁₂N₄, 99.8% Sigma-Aldrich), NaOH have been used. In the typical synthesis process, 0.05M copper acetate solution was prepared in distilled water while in a separate beaker 0.05M hexamethylenetetramine solution was prepared in deionized water under continuous stirring at ambient temperature. HMTA solution was added gradually into copper acetate under continuous stirring. Moreover, pH of solution was maintained about ~11-12 by adding NaOH solution. The resulting blue colour solution has been transferred into the Teflon flask at 95°C and system was aged for 24 hours. After completion of reaction black color precipitate was obtained which was further washed repeatedly with methanol and deionized water and dried at room temperature.

The structural properties of as grown microrods were examined by FE-SEM micrograph and X-ray energy dispersive spectroscopy (EDX). The crystal phase purity and crystallinity were examined by powder X-ray diffraction PXRD. The result shows the possible growth of highly crystalline CuO microrods.

4.3.3. RESULTS AND DISCUSSION
The synthesized 1D rods of CuO microstructures crystal phase and compositions were identified by X-ray diffractometer (XRD, Rigaku, operating at 40 kV and 20 mA using Cu Kα radiations, λ = 1.54178 Å with scanning rate 4°/min) in the range of 20–80°. The typical X-ray diffraction pattern of CuO was fully matched with monoclinic phase of CuO crystals JCPDS card number 05-0661 as shown in Figure 4.3.1. CuO crystal having monoclinic space group $C2/c$ ( $a = 4.68\text{Å}$, $b = 3.42\text{Å}$, $c = 5.1\text{Å}$ and $\beta = 99.54^o$). The two major peaks at 34.95° and 38.36° were
characteristic of pure monoclinic CuO crystals. There were no other peaks which could be responsible for presence of other oxides of copper (Cu\textsubscript{2}O and Cu(OH)\textsubscript{2}. The purity of the compound was further supported by energy dispersive spectroscopy (EDX) as shown in Figure 4.3.2, where Cu and O were found to be 55.29\% and 44.71 \% (1:1), respectively.
**Figure 4.3.1.** X-ray diffraction pattern of as synthesized CuO microstructure.

**Figure 4.3.2.** Energy dispersive X-ray spectrum of CuO microstructure.
The FE-SEM micrograph of CuO crystal is depicted in Figure 4.3.3. The low magnification image exhibits that the 1D microstructure has a center of origin and grown in cluster. The diameter of rods was constant from base to the tip i.e., CuO rods were grown uniformly and highly crystalline in nature. There were three different modes of attachment of rods; the short microstructures were attached to one another using their low Miller Indices crystal phase (100), (100) and (110) surfaces respectively. This type of crystalline growth has been well-defined in recent years and described as a cementing process or oriented attachment. As the rods were grown in cluster, so they were connected to each other from base of origin. It was interesting to observe in the high resolution image where the growths of 1D rods were viewed as a separate cluster without using any template. In addition to this, the length of rods was remaining almost constant throughout the diameter.
**Figure 4.3.3.** FE-SEM (a) low magnification image and (b) high resolution image of 1-D CuO Microstructure.
In typical experiment procedure, aqueous solution of 0.05M Cu(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O was mixed with equivalent concentration of HMTA. It was important to note that there was no immediate precipitation, but the clear light–blue colour of copper acetate turned into turbid solution. Moreover, pH of solution was maintained by using NaOH solution, which not only adjusts pH about ~11-12 of resultant solution but also plays an important part in the synthesis of microstructure of CuO. This observation suggested that in the initial stage Cu(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O is converted to Cu(OH)\textsubscript{2}. The sequential reactions involving are given below.

\[
\text{Cu(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 + 2\text{CH}_3\text{COONa} + 2\text{H}_2\text{O} \tag{4.3.1}
\]

At initial stage of the reaction, heat was evolved when NaOH was dissolved in the water that will facilitate the thermal degradation of HMTA. The HMTA get hydrolyzed and thus hydroxyl ions were generated.

\[
\text{(CH}_2\text{)}_6\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + 4\text{NH}_3 \tag{4.3.2}
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \tag{4.3.3}
\]

The formation of Cu(OH)\textsubscript{2} is very important for growth of CuO crystal which initially serves as building blocks for synthesis of microstructure of pure CuO. The Cu(OH)\textsubscript{2} has been further calcined at 400°C for 30 min. to convert Cu(OH)\textsubscript{2} to pure CuO crystals as shown in below reaction;

\[
\text{Cu(OH)}_2 \xrightarrow{\Delta} \text{CuO} + \text{H}_2\text{O} \tag{4.3.4}
\]

Hence, the described reactions explain the proper growth of CuO. Therefore, it is
expected that electrostatic attraction also play pivotal role in the uniform growth.

4.3.4. CONCLUSION

In summary, we successfully synthesized one dimensional CuO microstructures via simple hydrothermal process at 95 °C using copper acetate, hexamethylenetetramine and NaOH in water solvent. The detailed structural investigation reveals that the growth of microstructures were uniform and centre oriented, as the rods were grown in cluster so they were connected to each other from base of origin. One dimensional CuO exhibiting high surface area and hence provide an opportunity to use them for fabrication of efficient devices in near future.
References


Synthesis and Characterization of Nanocrystalline CdS, ZnS, and Cd<sub>x</sub>Zn<sub>1-x</sub>S,


